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WATERS FOR WATERFLOODING SAN JOAQUIN VALLEY, CALIF., PETROLEUM RESERVOIRS

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WATERS FOR WATERFLOODING SAN JOAQUIN VALLEY, CALIF., PETROLEUM RESERVOIRS

By G. L. Gates and W. H. Caraway

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WATERS FOR WATERFLOODING SAN JOAQUIN VALLEY, CALIF., PETROLEUM RESERVOIRS

by

G. L. Gates[1] and W. H. Caraway[2]

ABSTRACT

Five possible sources of water for waterflooding of petroleum reservoirs in the arid San Joaquin Valley of California were considered. Three of them (water produced with petroleum, water from a shallow saline aquifer, and waste irrigation water) were analyzed chemically; laboratory information for one (sea water) had been developed during a previous study. A series of laboratory tests made on the fifth source (fresh water) determined the solubility of calcium sulfate dihydrate in water. Laboratory analyses included the following: Chemical analyses of water produced with petroleum and waste irrigation water; solubility of calcium sulfate dihydrate in water and brines; the effect of excess sulfate on the solubility of calcium sulfate in brines; the presence of sulfate-reducing bacteria; and the permeability of cores from a petroleum reservoir to air, to water from other petroleum reservoirs, and to waste irrigation water. The results showed that most of the waters and mixtures of waters are compatible with petroleum reservoir waters and are generally suitable for injection. The calcium content of some of the formation waters is quite high, and care must be taken to prevent precipitation of calcium sulfate dihydrate. The permeability of the few cores tested was about the same to water and brines as to air, indicating that formation damage due to clay swelling will not be serious. The waters most likely to be available for injection are water produced with petroleum, water from shallow saline aquifers, and waste irrigation water.

INTRODUCTION

Secondary recovery of petroleum is growing in importance in the drive to supply the petroleum needed for our expanding economy. Because recovery by primary methods leaves 50 to 90 percent of the original petroleum in the reservoir, secondary methods have been developed to recover additional petroleum. Waterflooding has been used successfully, and its use is growing.

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Scott and Hawkins (17)[3] state: "By 1980 one of every three barrels of domestic crude produced will be from flood-pressure maintenance."

As shown in figure 1, the growth of waterflooding operations in California has been notable; from 1956 to 1967 the number of projects more than tripled. By December 1968, a total of 2,220,000 barrels of water was being injected per day into 176 pools (2). In the San Joaquin Valley, however, the number of active projects has increased more slowly, for obtaining injection water has been a problem.

This Bureau of Mines study was undertaken to determine the availability and suitability of various waters for injection and to determine whether certain waters that threaten to pollute fresh water supplies could be used for injection. The following possible sources of injection water were studied, but not all in the same detail: (1) Waters produced with petroleum; (2) waters from saline aquifers; (3) water drained from irrigated agriculture lands; (4) sea water; and (5) fresh water from natural runoff, shallow wells, and that which will be imported by a canal system now under construction.

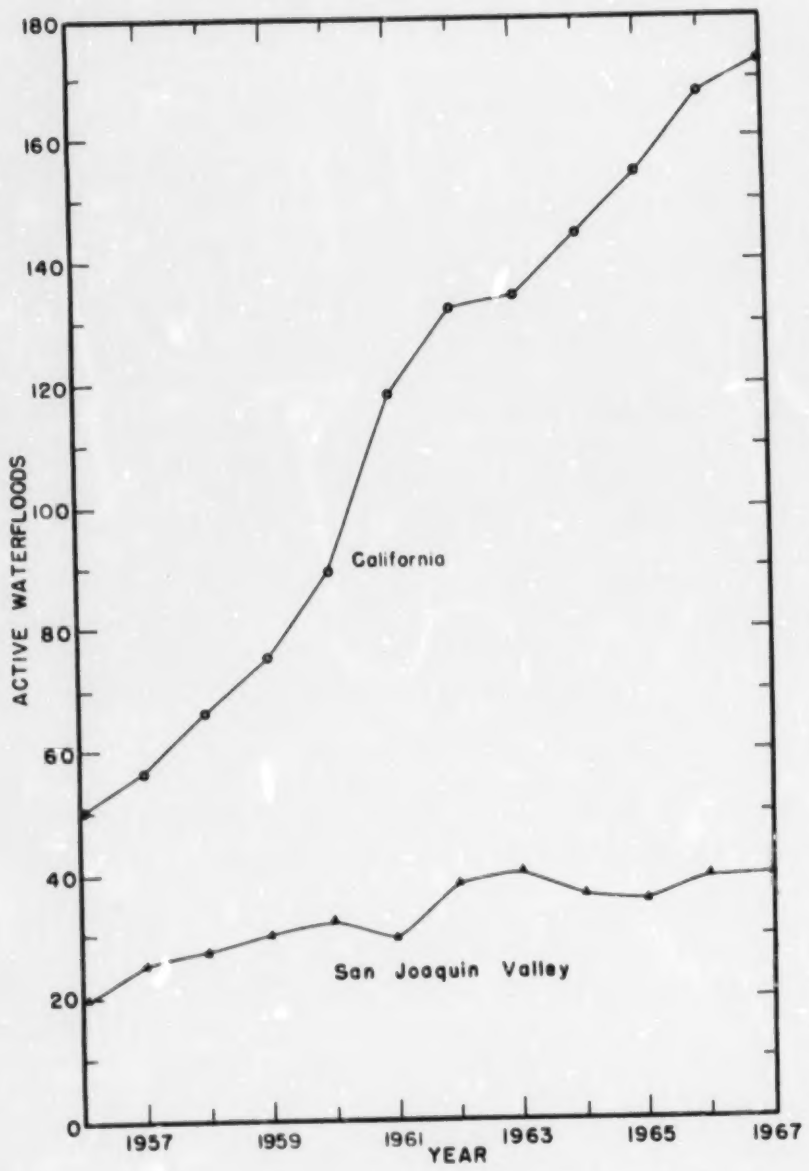

FIGURE 1. - Growth of Water Injection Projects in California.

Obtaining a suitable source of injection water is a problem anywhere, but the problem is compounded in the San Joaquin Valley by geography and location. The San Joaquin Valley is an arid region, and the sources of fresh water are limited. The valley, which is generally defined as the southern two-thirds of the Great Central Valley, extends from Stockton in the north to the foot of the Tehachapi Mountains in the south and east and west between the Sierra Nevada and the Coast Ranges. Surface

[3]Underlined numbers in parentheses refer to the list of references at the end of this report.

waters enter the valley in the Kern River, the California Aqueduct, the Friant-Kern Canal. The average Kern River flow has been about 667,000 acre-feet per year (1,400,000 bbl a day) (11).

The southern part of the valley is an important oil-producing area of the United States. As shown in table 1, the area produced more than 100 million barrels of oil in 1967, and reserves are estimated to be about 2 billion barrels. Because waterflooding will often recover as much oil as that produced by primary methods, the area will produce additional millions of barrels of oil in the future if adequate sources of water can be developed for injection into reservoirs.

ACKNOWLEDGMENTS

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VOLUMES OF WATER REQUIRED FOR FLOODING

Large volumes of water are required to move oil to production wells during waterflood operations. The largest volume of water is required during the fill-up period; the injection rate during fill-up may be twice as large as that required after the pore volume previously occupied by gas has been filled.

Reported water requirements (3) indicate that during the fill-up period an injection rate of 1 to 2 bbl per day per acre-foot of depleted reservoir is desirable. After fill-up, the rate should be maintained at about 1, but not less than one-half, bbl per day per acre-foot. If the oil-producing sand is in contact with a gas sand above or a water sand below, the water requirements normally will be several times those needed for the oil sand alone. Gas sand fill-up requirements per acre-foot may be 3 or 4 times those of oil sand. Estimates should also include some migration of water into the water sand. Experience indicates that the water volume needed will vary from 150 to 170 percent of the total pore volume (3).

A compilation was made of the major fields in the San Joaquin Valley that produce oil having an API gravity in the range of 13.5° to 41°. These fields and gravities are listed in table 1, together with data on water produced and injected, oil produced, and estimated reserves. These data show that more water is being produced from these fields than is being injected, but not many of the fields are being flooded at this time. Data on two large, successful waterfloods outside the valley (Dominguez and Wilmington) show that when fields are being waterflooded, considerably more water is injected than is produced.

TABLE 1. - Major San Joaquin Valley fields containing oil with average API gravity greater than about 20°, 1967

Field	Water produced,[1] bbl	Water injected,[1] bbl	Oil produced,[1] bbl	Reserves,[2] bbl	Gravity,[1] ° API
Ant Hills	2,170,000	2,083,575	173,800	([3])	13.5
Antelope Hills	2,176,000	([3])	402,400	([3])	17.5
Asphalto	3,220,000	([3])	3,154,600	30,295,000	34.2
Belgian Anticline	1,410,000	([3])	714,900	([3])	35
Bellevue	371,000	([3])	75,200	([3])	35
Bellevue West	515,000	([3])	110,700	([3])	35
North Belridge	1,789,000	([3])	400,100	([3])	37
Brentwood	1,528,000	([3])	552,500	([3])	38
Buena Vista	16,475,000	4,962,031	6,555,900	72,244,000	30
Canal	702,000	1,710,444	696,400	([3])	35
Canfield Group	1,664,000	([3])	993,800	([3])	32
Coalinga Eastside	16,298,000	20,085,000	4,802,200	72,244,000	23
Coalinga East Extension	11,601,000	([3])	8,029,000	85,703,000	37
Guijarral Hills	423,000	([3])	687,200	([3])	37
Jacalitos	347,000	26,820	180,300	([3])	30
Coles Levee North	466,000	3,599,416	1,907,900	28,292,000	38
Coles Levee South	57,000	0	464,900	([3])	36
South Cuyama	13,863,000	12,994,530	5,041,500	39,783,000	32
Russel Ranch	9,134,000	10,240,088	819,100	([3])	34
Edison	15,211,000	315,680	2,029,200	17,037,000	25
Elk Hills	8,962,000	3,180,041	1,567,700	1,024,853,000	30
Helm	7,455,000	([3])	648,800	([3])	33
Raisin City	22,257,000	([3])	776,700	([3])	23
Riverdale	3,923,000	([3])	248,900	([3])	35
Fruitvale	9,239,000	169,067	1,533,500	11,254,000	21
Greeley	4,488,000	3,706,667	1,948,800	14,285,000	38
Kettleman Hills North	6,276,000	273,674	1,446,400	24,203,000	36
Lost Hills	12,381,000	2,331,023	2,596,000	24,702,000	21
McDonald Anticline	984,000	([3])	727,000	([3])	28
McKittrick	6,188,000	([3])	11,140,700	90,640,000	30
Midway Sunset	63,179,000	1,508,947	29,346,500	192,640,000	20
Mountain View	3,352,000	397,144	976,300	([3])	30
Paloma	39,000	([3])	116,100	([3])	40
Pleito	72,000	50,779	108,300	([3])	20
Railroad Gap	1,388,000	([3])	1,137,200	10,169,000	32
Rio Bravo	4,302,000	4,241,795	1,260,000	16,175,000	41
Rosedale	644,000	434,865	61,300	([3])	31
Rosedale Ranch	5,998,000	5,264,248	537,600	([3])	20
Round Mountain	54,745,000	([3])	911,700	12,504,000	18
San Emidio Nose	743,000	394,359	662,800	([3])	31
Strand	1,011,000	([3])	313,800	([3])	32
Tejon Grapevine	4,733,000	2,565,813	608,900	([3])	22
Tejon Hills	3,270,000	1,746,449	141,000	([3])	29
Tejon North	548,000	([3])	519,600	([3])	40
Ten Section	1,249,000	503,772	1,369,300	14,620,000	35
Vallecitos	312,000	18,293	80,200	([3])	36
Wheeler Ridge	1,442,000	1,108,929	1,482,400	10,865,000	30
Total	328,600,000	75,433,584	100,059,100	1,792,508,000	-
ACTIVE CALIFORNIA WATERFLOODS OUTSIDE SAN JOAQUIN VALLEY					
Wilmington	173,816,000	298,792,069	58,942,700	([3])	23
Dominguez	24,257,000	27,752,261	2,762,100	([3])	30

[1]Conservation Committee of California Oil Producers. Annual Review of California Oil and Gas Production 1967.

[2]As of Jan. 1, 1968. Oil and Gas J., v. 66, No. 6, Feb. 5, 1968, p. 161.

[3]Not available.

The number of active waterfloods in the valley will probably increase in the future. Based on experience in other California waterfloods, it is estimated that a peak of about 300,000 bbl per day of supplemental water will be needed in the future to waterflood fields in the San Joaquin Valley that produce oil having an API gravity similar to those listed in table 1.

SOURCES OF WATER FOR WATERFLOODING

As mentioned before, several different sources of water were considered for injection in San Joaquin Valley oilfields. In some cases, it was found that sufficient information was available from previous research done in our laboratory, or from the literature, so that no additional laboratory experiments were needed. In other cases, however, it was found that problems arose that could only be answered by laboratory analyses; in these cases, the analyses were made and are reported in the following sections.

Water Produced With Petroleum

Water produced with petroleum is often an excellent flood water. Because it has been in contact with the reservoir rock and is in equilibrium with the chemically active clay minerals in the formation, it usually will not cause any change in the permeability of the formation when injected. Additionally, if such produced waters are kept in a closed system, they will be free from suspended solids and dissolved oxygen. However, appreciable quantities of oil must be removed from these waters before injection; this is usually done by filtration or gravity separation (25).

In treating California oilfield waters for waterflooding, caution should be used because many of these waters contain appreciable quantities of salts of organic acids (8). When California brines associated with crude oils are acidified, an oil layer of organic acids may separate from the brines.

Complete chemical analyses of possible injection waters are needed in order to predict reactions that may take place when these waters are mixed with water from any other sources. Such analyses were not available for most of the produced waters in the area, so representative samples were collected and analyzed in the laboratory. The methods and procedures used have been described in previous publications (7). The results of these tests are summarized in table 2 and will be further discussed in the section of this report concerning the mixtures of reservoir waters and waste water from irrigation.

Water From a Saline Aquifer

Waters from saline aquifers are used to waterflood many oilfields in the United States where they are suitable in both quantity and quality. Such waters often have many advantages, among which are proximity of source to injection well, ease of water treatment, an expandable supply, and, sometimes, the use of abandoned oil wells for water supply wells.

TABLE 2. - Chemical composition of produced and waste waters

Sample	Sample field	Source formation or area	Milligrams per liter											Organic acids, mg mol per liter[1]
			Ca	Na	Ba	Sr	Mg	K	SO_4	Cl	CO_3	HCO_3	Total solids	
WATERS PRODUCED WITH PETROLEUM AND FROM AQUIFERS														
1F	Kettleman Hills	Temblor.....	2,280	9,440	1.2	64.9	92.2	113	320	17,180	0	102	33,270	24.7
13F	...do.....	...do.....	3,500	6,520	1.4	89.4	18.8	83	329	15,830	0	125	28,500	14.3
11F	North Coles Levee.	Stevens.....	491	9,030	5.3	54.4	53.3	123	11	13,360	0	260	25,870	46.4
12F	...do.....	...do.....	518	8,900	7.7	55.8	59.0	117	15	13,820	0	319	26,610	43.9
2F	E. Coalinga Sec. 11A.	Santa Margarita.....	32	1,570	.1	1.7	21	9	2,610	315	0	312	4,825	.2
3F	...do.....	Temblor.....	49	1,530	2	2.8	112	25	1,530	249	0	256	4,605	.7
4F	Buena Vista Hills.	555 Stevens.....	74	10,300	7.7	22	31	75	21	13,920	0	1,680	28,110	26.6
5F	...do.....	11D Unit.....	478	11,600	3.5	16	538	200	0	19,740	0	1,100	34,390	.8
6F	Kerto 5K.....	-	245	9,160	8.3	23	270	82	9	14,430	0	1,920	26,660	.0
7F	NW Mtn. View...	Chanac, Transition, and Santa Margarita	496	2,290	1	10	110	22	0	4,045	0	272	7,317	.0
14F	1-C Buena Vista	Tulare.....	209	2,770	.1	3.2	147	15	1,690	3,720	0	106	8,976	2.4
8F	...do.....	...do.....	219	2,720	0	7.2	236	17	1,570	3,710	0	232	9,101	.1
9F	Elk Hills.....	Shallow zones.....	1,307	10,070	2.9	16	546	76	14	20,700	0	118	35,370	.8
10F	Greeley.....	Vedder zone.....	271	8,110	0	19	50	135	32	12,350	0	260	22,500	16.0
WASTE IRRIGATION WATERS														
1a	Firebaugh.....	-	532	861	0.4	2.8	172	4.7	2,290	593	0	267	4,997	0.0
1b	...do.....	-	514	651	-	2.7	184	4.1	2,180	415	0	213	4,384	.0
2a	South Dos Palos	-	558	1,880	1.5	1.2	36	2.3	3,860	1,440	0	366	8,940	.3
2b	...do.....	-	648	2,720	-	11.2	413	3.2	5,230	2,130	0	307	12,090	.0
3a	Firebaugh.....	-	331	2,940	0	.4	318	2.3	5,900	894	0	326	10,850	.0
3b	...do.....	-	419	6,394	-	.0	381	2.5	11,980	2,165	0	556	21,790	.0
4a	...do.....	-	257	1,870	.8	.5	269	2.3	3,980	639	0	127	7,706	.2
4b	...do.....	-	404	1,770	-	3.0	187	6.9	3,910	645	0	378	7,506	.0
5	Corcoran.....	-	263	781	-	3.3	94	9.6	1,120	501	0	615	3,020	.0
6	...do.....	-	167	1,290	-	4.2	76	14.4	1,330	817	0	603	3,958	.0
7	Wasco.....	-	222	1,310	-	4.9	22	6.6	1,480	616	0	615	3,788	.0
8	Corcoran.....	-	207	1,270	-	3.0	18	7.3	1,800	559	0	622	3,758	.6
9	...do.....	-	354	5,800	-	1.4	534	19.6	11,110	2,510	0	619	20,980	.0
10	...do.....	-	242	150	-	3.3	40	9.2	790	215	0	355	1,506	.2

[1]Calculated from sodium hydroxide titration assuming a valence of 1.

In the San Joaquin Valley, the Tulare Formation may be a good source of water. In fact, it has been found to be a good source in a few wells in the southern end of the valley. The most extensive confined aquifer is the system overlain by the Corcoran Clay Member of the Tulare Formation, which covers more than 5,000 square miles. However, the volume of water available from the whole area is not known.

Although the volume of water obtained from the Tulare was adequate in the well that was sampled, wells in other areas must be tested to be sure that an ample volume of water is available. In the northern part of the valley, water from the Tulare Formation in the Kettleman Hills field is classified as fresh water (20). However, in the southern portion, the water is saline, as shown in table 2.

Analyses of Tulare Formation water samples obtained in the Buena Vista field are shown in table 2. This water is low in calcium and barium content, but high in sulfate. It does not require filtration and is low in dissolved gases, particularly oxygen, which may cause corrosion. If the waters already in the formations to be flooded are high in calcium or barium content, the possible precipitation of barium sulfate or calcium sulfate would have to be considered.

One problem that must be taken into account when considering withdrawal of subsurface water is the possibility that such withdrawal may cause the surface to subside. Such subsidence often accompanies withdrawal of fluids from unconsolidated formations in California whether the withdrawal is from shallow fresh-water sands or deep, oil-bearing sands.

The possibility of subsidence does not, by itself, eliminate from consideration water from the Tulare or similar formations as a source of injection water. This is one of the factors, however, that must be given close scrutiny before full-scale development is started.

Extensive land subsidence has occurred in the valley as the result of intensive pumping of ground water and flooding the surface for irrigation (15, 23-24). Maximum subsidence has ranged from 8 feet south of Bakersfield to about 23 feet southeast of Los Banos. Subsidence may cause serious problems in construction and maintenance of structures in the area.

Waste Irrigation Water

The irrigated lands of the valley, in common with arid lands everywhere, contain several kinds of soluble salts, and after several years of irrigation, these salts accumulate near the surface and interfere with the growth of many crops. To alleviate this problem, tile drains are buried in the fields so that the water then moves downward and carries the soluble salts in solution through the tile drains and into a larger canal drainage system. This continual installation of tile drains, together with the ever-increasing acreage of land under irrigation, will produce ever-larger volumes of waste water in the future, as shown in table 3. If a considerable part of this waste water could be injected into oil reservoirs, a potential pollutant would then become a valuable asset.

TABLE 3. - Estimated quantity and dissolved solids of waste waters[1]

Area	1970			1980		
	Volume		Dissolved solids, ppm[3]	Volume		Dissolved solids, ppm[3]
	Bbl per day	Acre ft per year[2]		Bbl per day	Acre ft per year[2]	
Nonlake bed, lower Kings River Conservation District.....	110,000	5,300	4,000	310,000	14,600	2,800
Lake bed, lower Kings River.....	540,000	25,600	6,900	1,300,000	62,600	2,700
Sand Ridge.....	0	0	0	21,000	1,000	9,300
Buena Vista Lake..	0	0	0	130,000	6,200	7,500
Total.....	650,000	30,900	-	1,761,000	84,400	-
	1990			2000		
	Volume		Dissolved solids, ppm[3]	Volume		Dissolved solids, ppm[3]
	Bbl per day	Acre ft per year[2]		Bbl per day	Acre ft per year[2]	
Nonlake bed, lower Kings River Conservation District.....	516,000	24,300	2,600	650,000	30,700	2,400
Lake bed, lower Kings River.....	1,860,000	87,400	3,700	2,070,000	97,200	3,600
Sand Ridge.....	320,000	15,100	5,600	1,020,000	47,800	4,600
Buena Vista Lake..	308,000	14,500	4,800	508,000	23,900	4,000
Total.....	3,004,000	141,300	-	4,248,000	199,600	-

[1]California Department of Water Resources (13).
[2]Acre ft per year values for beginning of decade.
[3]Ppm values for decadal mean except year 2000.

The waters from the drains are scattered over a large area, and it would be prohibitively expensive for a company to collect them for waterflooding. The problems of collecting the waters and making them available at a location close to the oilfields will be solved if the proposed San Joaquin Valley master drain (13) is completed as planned. This drain, shown in figure 2, will transport waste irrigation waters to San Francisco Bay and will pass close to many of the large oilfields in the valley. The first portion will extend from Kettleman City to the Bay area. It will include storage facilities and be operational in 1971. A second portion will extend from the Buena Vista Lake area between Bakersfield and Taft, near the South Coles Levee field, to Kettleman City. The whole drain will be about 280 miles long and cost about $100 million. Waste water production will be seasonal; however, storage basins, which are planned as part of the drain system, will insure a supply of water during the nonirrigation periods in the winter months.

To learn the composition of waters drained from fields, 10 samples were collected under controlled conditions from the six locations listed in table 2. The samples were analyzed in the laboratory using standard wet chemical methods and a flame photometer (7). The results show that these waters

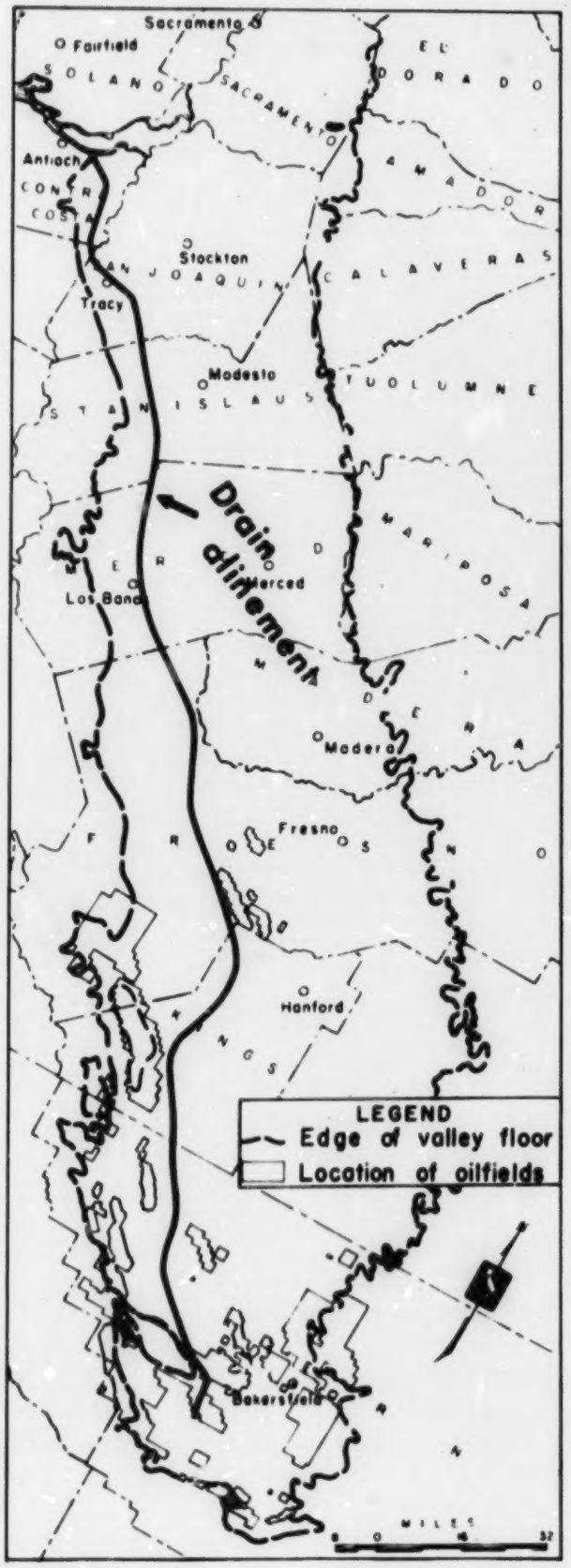

FIGURE 2. - Location of San Joaquin Master Drain and Oilfields.

contain primarily sodium sulfate, with minor amounts of calcium, magnesium, and chloride. Because the barium content of oil formation waters in the valley is low, barium sulfate scaling would not be the problem in this area that it is in the Wilmington field, where ocean brines are used for waterflooding (5-6).

Sulfate-Reducing Bacteria

Sulfate-reducing bacteria in injection water are usually harmful because they multiply in the reservoir and release hydrogen sulfide. This poisonous gas not only causes severe corrosion of production equipment, but it also reduces the value of produced oil and gas.

To determine the presence or absence of sulfate-reducing bacteria in waste irrigation waters, samples were obtained and evaluated by the method recommended by the American Petroleum Institute (1). Samples from four locations were obtained from draintiles or sump-pump discharges to insure that those used in the test were fresh. Only one sample, taken from a ditch, contained minute evidence of sulfate-reducing bacteria. Sulfate-reducing bacteria, therefore, should not be a serious problem when waste irrigation waters are used for waterflooding.

Dissolved Oxygen Content

The oxygen content of certain waters being considered for injection must be determined because oxygen in the water causes severe corrosion of metal equipment and plugging of injection wells with rust. Oxygen removal is an expense that is often avoided by using water produced with petroleum or from saline aquifers but may be an important item in the consideration of waste irrigation water. Data collected by the California Department of Water Resources on the oxygen content of drain water are given in table 4, and their method of sampling follows.

TABLE 4. - Dissolved oxygen in San Joaquin Valley waste irrigation waters

Water source	Number of samples	Dissolved oxygen content, ppm			Standard deviation
		Maximum	Minimum	Average	
Tile outlet.....	26	7.9	0.7	4.4	2.25
Sump.....	12	8.3	2.0	6.0	1.89
Pump discharge.....	11	9.5	3.2	6.7	1.62

Samples were collected from three points in the drainage system: At the outlet from the underground tile (tile outlet), from the sump into which the water from the tile drains, and at the pump discharge. (A pump lifts the water up to a canal or reservoir.) Every effort was made to exclude contact with the air, and the readings were made quickly. The tile outlet was sampled using a rigid, 1/2-inch plastic tube, which collected the sample 6 feet upstream from the tile outlet. Samples of sump waters were obtained by submerging a dissolved-oxygen sampling bottle or a bucket; pump discharge samples were also collected in the dissolved-oxygen bottle. The water sometimes fell as much as 6 feet from the tile outlet to the sump, thus exposing the water to additional oxygen. This may account for the higher values, given in table 4, of dissolved oxygen in the sump and pump discharge than in the tile drain itself.

Waste Irrigation Water Summary

It now appears that waste irrigation water will be available in sufficient volume in the future to supply water for waterflooding most of the oilfields close to the master drain system. The quality of this water is generally good, but some treatment will be needed, especially to remove suspended solids and dissolved oxygen. This drain water may prove to be one of the least expensive sources of injection water in the valley.

Sea Water

No consideration of waters potentially available for injection in the valley would be complete without mentioning the largest water source of all--the Pacific Ocean. Sea water was analyzed extensively in our laboratory in previously reported studies (5-6); therefore, no additional analyses were necessary for the present study.

The chemical composition of waters from saline aquifers and irrigation waste were found to be similar to that of sea water--there are some differences, but chemical composition probably will not be the deciding factor. A pipeline about 125 miles long would be needed to bring sea water to the valley. When all factors are considered, it does not seem probable that sea water will be able to compete with other sources as the best source of injection water.

Fresh Water

Surface water provides a cheap and reliable source of water for injection in many parts of the country, but in the San Joaquin Valley the supplies of

fresh water are limited. The main surface supplies are the Kern River, the California Aqueduct, and the Friant-Kern Canal, but these are not sufficient to meet the demand for both domestic use and irrigation. Consequently, huge volumes of ground water have been withdrawn in the past 40 years through about 50,000 wells; most of this shallow subsurface water is used for irrigation.

Because of the shortage of fresh water in the valley and southern California, the California Water Project is being constructed to bring additional water to these areas. One of the main canals of the system, the California Aqueduct, will follow the western edge of the valley and pass close to many of the major oilfields. Water in this canal will reach the southern end of the valley by 1971.

Even with the completion of this huge project, however, it is not certain that water will be available for waterflooding. It is reported by Jensen (9) that surplus water can be purchased for waterflooding, but that some of the water districts that have contracted for water from the project have indicated that their agricultural water is entirely committed for the forseeable future. This indicates that in many of the water districts in the valley it is improbable that there will be surplus water available to the oil industry for waterflooding.

MIXTURES OF RESERVOIR WATERS AND FLOOD WATERS

When waters associated with petroleum in the reservoir rocks are sufficiently mixed with certain flood waters, insoluble solids may be formed. These may adversely affect the permeability of the reservoir rocks. The extent of the mixing of interstitial waters with injected waters within the formation is not well understood. Some engineers believe that liquids are displaced in porous formations with efficient pistonlike action so that mixing and subsequent precipitations within the pores do not occur. However, others believe that the mixing is sufficient to form harmful solids during flow in the formations. Conflicting information and opinions regarding possible damage make reliable conclusions difficult. Recent laboratory studies with sand-packed columns showed that barium and calcium sulfate precipitates did not cause measurable permeability reduction. In contrast, ferric hydroxide precipitate formed from mixing solutions in sand columns did cause serious loss of permeability (22). Apparently, in some conditions, mixing is sufficient to cause serious reduction of permeability; whereas, mixing is not sufficient to be harmful in other conditions. Significant field observations are needed in this problem.

Examination of the chemical composition of waters shown in table 2 indicates that calcium sulfate might be expected to precipitate from mixtures of certain formation waters high in calcium and waste irrigation water high in sulfate. A survey of previously published information regarding the solubility of calcium sulfate in brines (10, 12, 14, 16, 18-19, 21) indicated that the most probable precipitate would be calcium sulfate dihydrate (gypsum). Fulford (4) found that a decrease in pressure increased scale deposition, and an increase in sodium chloride concentration decreased deposition. The crystal form of calcium sulfate precipitated from brines in this study at

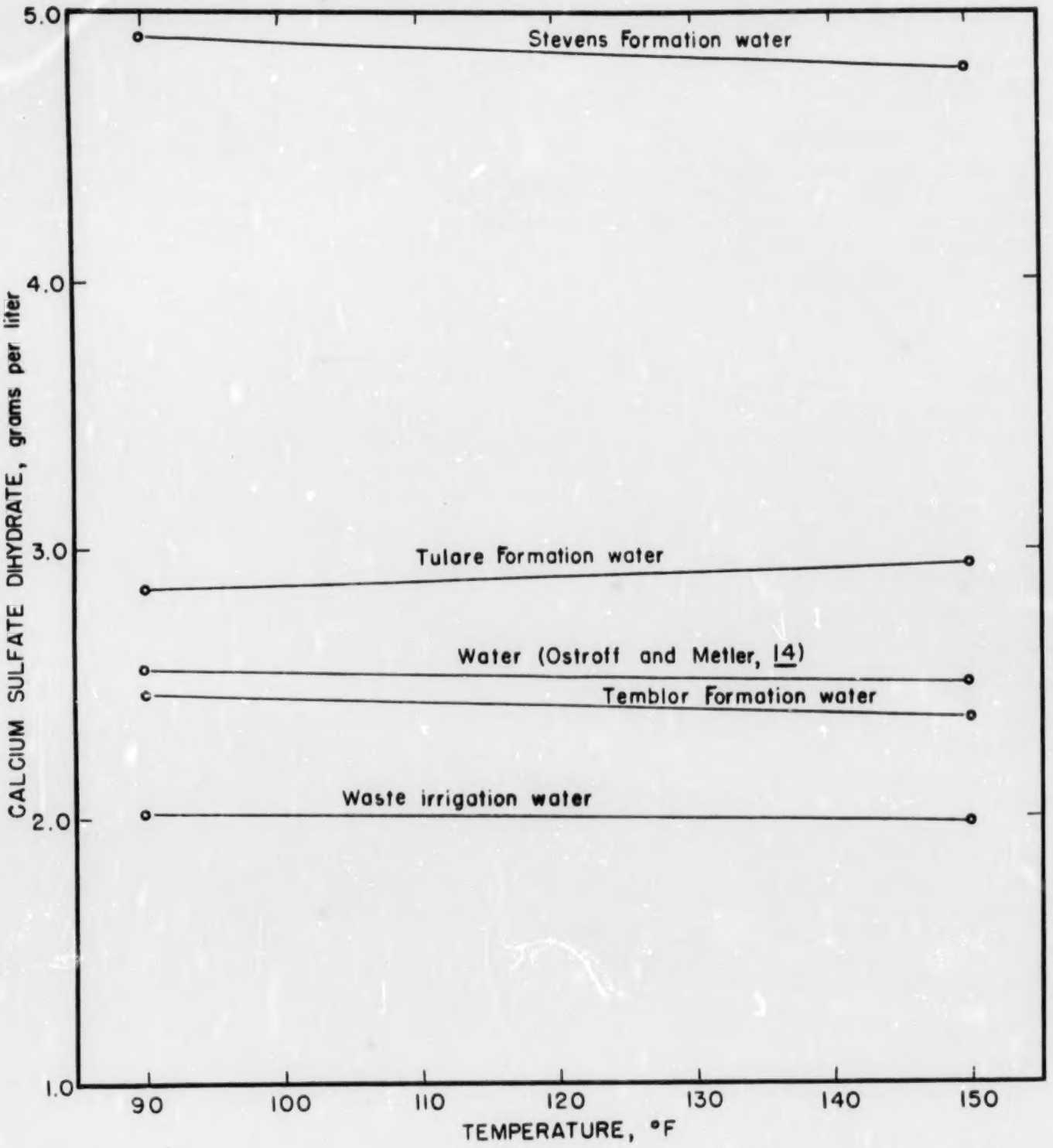

FIGURE 3. - Effect of Temperature on the Solubility of Calcium Sulfate Dihydrate in Water and Brines.

temperatures below about 180° F was the dihydrate. The crystal form was identified by means of differential thermal analysis.

The solubility of calcium sulfate dihydrate in distilled water, 0.43N sodium chloride, Kettleman Hills-Temblor Formation water, North Coles Levee-Stevens, Tulare injection water, and waste irrigation waters at 90° F was determined. The results are shown in table 5 and figure 3.

TABLE 5. - Solubility of calcium sulfate dihydrate in water and brine, 90° F, mg per liter

Water	0.43N NaCl	Kettleman Hills-Temblor Formation	North Coles Levee-Stevens Formation	Buena Vista-Tulare 1C	Waste irrigation	
					Corcoran	Firebaugh
2,850	4,850	2,450	4,910	2,850	2,020	2,190

As shown in figure 3, no significant differences in calcium sulfate dihydrate solubility was found at 90° and 150° F in the oilfield brines and waste irrigation waters. Because of the uncommon-ion effect, the solubility of calcium sulfate dihydrate in sodium chloride brines (Stevens Formation brines) was approximately 5 grams per liter. This value is about double that found in distilled water and brines containing an excess of sulfate.

Mixtures of Kettleman Hills-Temblor water and waste irrigation water (sample 9, very high in sulfate) were studied. The solutions were mixed at 90° F for 2 to 4 weeks. This mixture and other mixtures more representative of the average irrigation waters were studied in the same manner. The results showed very little reaction between the waters studied. Only one mixture, samples 13F and 9, was saturated with calcium sulfate, and no calcium sulfate crystals were observed. However, a very small quantity of solids was filtered from the mixtures, indicating the desirability of filtering floodwaters. The solids filtered from solution were apparently primarily organic matter, which may have been organisms that grew in the solutions in light.

EFFECT OF EXCESS SULFATE ON CALCIUM SULFATE DIHYDRATE SOLUBILITY

The use of floodwaters containing large quantities of sulfate raises the question of the effect of excess sulfate on the solubility of calcium sulfate in these brines. A series of tests, in which concentrated sodium sulfate solution was added to the brines, was run to determine this effect. The solutions were mixed for about 30 days to insure equilibrium, and then the calcium and sulfate concentrations were determined.

The results of the tests are shown in table 6 and in figure 4. Figure 4 shows that the Kettleman Hills-Temblor Formation water initially contained about 3,500 mg of calcium per liter of water and 350 mg of sulfate per liter. At a concentration of about 1,600 mg of sulfate per liter of solution, the brine was saturated with calcium sulfate dihydrate, and precipitation occurred. Further addition of sulfate reduced the solubility of calcium sulfate dihydrate to about one-third of the initial value, and additional precipitation occurred.

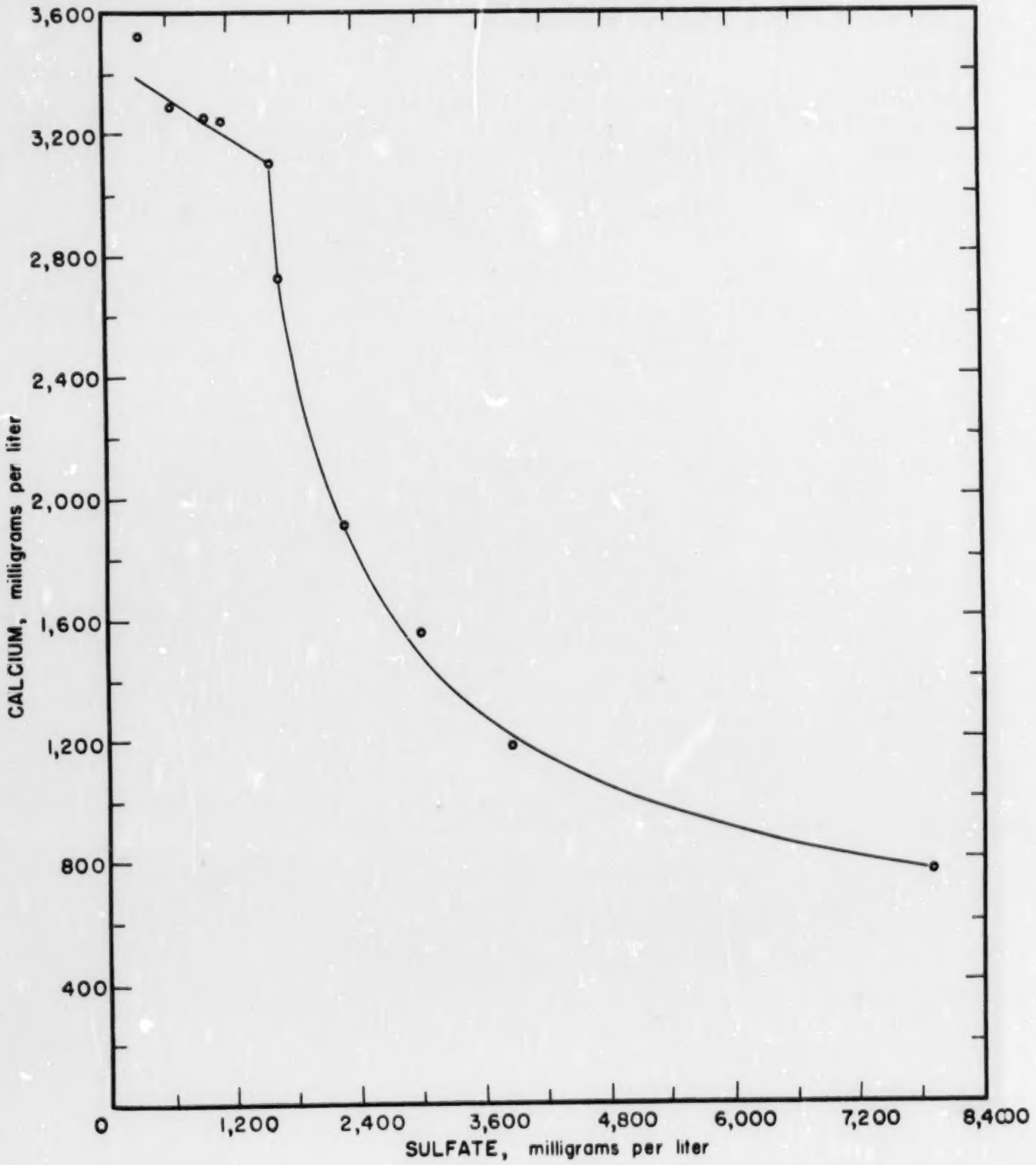

FIGURE 4. - Relation of Calcium to Sulfate Per Liter of Brine.

TABLE 6. - Effect of sulfate on the solubility of calcium sulfate dihydrate in Temblor brine

Sulfate added, mg per liter	Sulfate in solution, mg per liter	Calcium in solution, mg per liter	Calcium sulfate dihydrate precipated, mg calculated
0	349	3,520	Undersaturated.
300	639	3,290	Do.
600	860	3,250	Do.
900	1,110	3,240	Do.
2,000	1,580	3,100	1,800
3,200	1,650	2,720	3,440
6,000	2,240	1,910	6,920
8,000	2,980	1,560	8,420
10,000	3,840	1,180	10,100
16,000	7,940	768	11,800

The solubility of calcium sulfate dihydrate was notably low in Kettleman Hills-Temblor water because of the excess calcium present. Likewise, it was low in Tulare Formation injection water and waste irrigation waters because of the excess sulfate present, as shown in table 2. Solubility was relatively high in North Coles Levee-Stevens Formation water because no excess of either calcium or sulfate was present, but the high sodium chloride content increased the solubility of calcium sulfate dihydrate.

PERMEABILITY OF ELK HILLS CORES TO WASTE IRRIGATION WATER

The effect of waste irrigation waters on the permeability of three cores from a San Joaquin Valley field (Elk Hills) was studied. The results (table 7) show that the permeability to waste irrigation water was only slightly less than the permeability to formation water.

After air permeability measurement, cores from the Elk Hills field were saturated with formation water and stored for 2 weeks to insure complete clay hydration. After the permeability determination to the formation water, the water was displaced with waste irrigation water, and 2 weeks later the permeability to waste irrigation water was determined.

TABLE 7. - Permeability of Elk Hills cores to air and brines, millidarcys

Air	Brine				Well	Depth, feet
	North Coles Levee	Elk Hills Shallow	Kettleman Hills-Temblor	Irrigation waste, Corcoran, Calif.		
1,700	-	620	-	570	42-16G	4,451
250	160	-	-	150	348-XR	6,220
-	-	-	120	140	372-35R	[1]6,801

[1]Core cut and stored in oil.

SUMMARY

The results of this study indicate that waters for waterflooding in the San Joaquin Valley fields may be obtained from waters produced from the oil reservoir, from shallow saline aquifers, and waste irrigation waters.

The shallow saline waters were generally good quality, but the quantity available has not been proven in many areas of the San Joaquin Valley. Waste irrigation waters are expected to be available by 1975 in ample quantities. Laboratory tests indicated that the quality is good, with the exception that gypsum-scale deposition may occur in a few operations. The waste waters were shown to contain appreciable quantities of sulfate. When mixed in the laboratory with one formation water that was unusually high in calcium, a saturated calcium sulfate solution was obtained. However, all other mixtures of waste irrigation waters with the formation waters studied were not saturated with calcium sulfate and were satisfactory. Limited permeability tests indicated that permeability of formation cores to waste waters was about the same as that measured with formation waters.

The use of waste waters for waterflooding operations would accomplish simultaneously two objectives. First, additional petroleum would be recovered, and second, a waste product that must otherwise be removed would be partially used locally for an economic gain.

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